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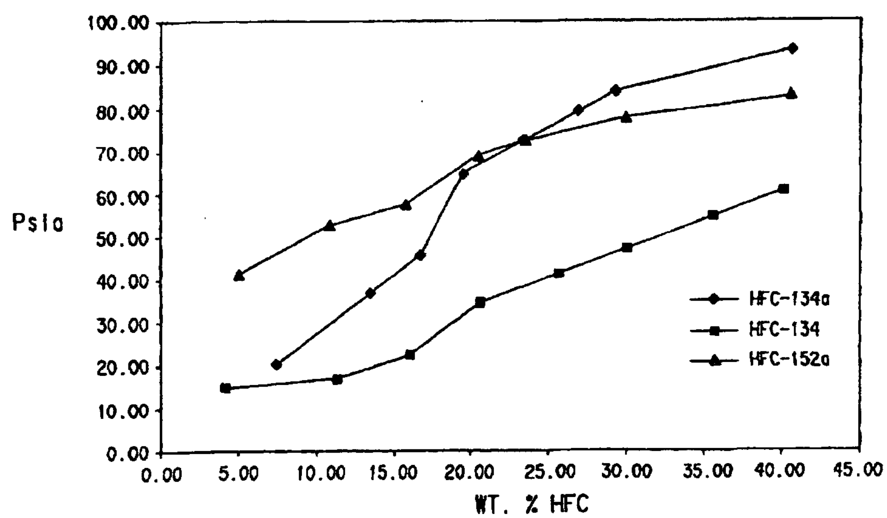

(57) Abstract

Blowing agent, active hydrogen-containing compositions, commonly referred to as B-side compositions or blends, and their use for the production of polyurethane and polyisocyanurate foams are disclosed. More particularly, the disclosure relates to blowing agent blend, foaming process and polyisocyanate-based foams which utilize environmentally friendly blowing agent compositions comprising a major proportion of 1,1,2,2-tetrafluoroethane (HFC-134).

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TITLE

Blowing Agent Blends and Use Thereof in the Preparation of Polyisocyanate-Based Foams

CROSS REFERENCE TO RELATED APPLICATIONS

This application claims the priority benefit of U.S. Provisional Application 60/022574. filed July 24, 1996.

FIELD OF THE INVENTION

The instant invention relates to compositions comprising a blowing agent and an active hydrogen-containing compound, commonly referred to in the art as B-side compositions or blends. and using such compositions for producing polyurethane and polyisocyanurate foams. More particularly, the instant invention relates to such blends, foaming processes and polyisocyanate-based foams which utilize environmentally friendly blowing agent compositions comprising a major proportion of 1,1,2,2-tetrafluoroethane (HFC-134).

BACKGROUND OF THE INVENTION

Polyisocyanate-based foams are well known in the art in a variety of forms for a variety of purposes, including, for example, as roofing and siding insulation in building construction, and as insulation in the manufacture of domestic and industrial refrigerators and freezers. The foams are typically produced by reaction of a polyisocyanate with an active hydrogen-containing material, usually a polyol, in the presence of a blowing agent. Historically, volatile chlorine-containing halocarbons have been the blowing agents of choice, especially fluorotrichloromethane (CFC-11). These materials, however, are being phased out for their possible involvement in affecting the stratospheric ozone and a perceived global warming effect on the environment.

Smits et al., U.S. Patent No. 4,997,706, disclose rigid closed-cell polyisocyanate-based foams having reduced thermal insulation loss prepared by reaction of a polyisocyanate with an active hydrogen-containing compound in the presence of both (a) a C_2 - C_6 polyfluorocarbon containing no Cl or Br atoms as blowing agent and (b) a blowing agent precursor, more specifically water, which provides CO_2 in situ, as co-blowing agent, through reaction with isocyanate groups of the polyisocyanate. The proportions of the polyfluorocarbon and the blowing

agent precursor are such that the initial gas composition within the closed cells of the foam comprise from about 1 to 60 mole percent polyfluorocarbon and from about 40 to 99 mole percent CO_2.

Similarly, Grunbauer et al., U.S. Patent No. 4,972,003, prepare rigid closed-cell polyisocyanate-based foams using gaseous blowing agents, broadly including HFC-134, HFC-134a and HFC-152a in conjunction with about 25-95 mole percent, based on the total moles of blowing agent, of a gas, e.g., CO_2, generated from a blowing agent precursor, e.g., water. The blowing agent composition may be employed as a preblend with an active hydrogen-containing reactant for the polyisocyanate.

The Smits et al. and Grunbauer et al. foaming systems suffer in that they require large proportions of water as a blowing agent precursor. This is not only wasteful of isocyanate (-NCO) groups, which react with water to produce CO_2, but tends to lead to unsatisfactory foam, e.g, refer to U.S. Patent Nos. 5,164,419 and 4,943,597.

The disclosure of the aforementioned patents, patent applications and publications is hereby incorporated by reference.

SUMMARY OF THE INVENTION

There is a need in this art for compatible blends of low-boiling blowing agents and active hydrogen-containing compounds wherein the blowing agents exhibit high solubility in the active hydrogen-containing medium; yet, exerts vapor pressures over the resulting blends that are sufficiently low that the blends need not be unduly pressurized before and during reaction with the polyisocyanate reactant. In general, the higher the blowing agent concentration, the lower the density of the foam produced. Also, the lower the vapor pressure of the blowing agent, when in combination with the active hydrogen containing component, the less difficult it is to provide for both a homogeneous reaction mixture with the polyisocyanate and a uniform cellular structure of the resulting foam. A need exists, therefore, for effective blowing agents for polyisocyanate-based foams that are environmentally friendly, that is, have substantially zero ozone depletion potential (ODP); furthermore have no or very low global warming potential (GWP), i.e., make no significant contribution to the so-called greenhouse effect, and preferably are substantially nonflammable for added safety in use. The instant inventions solves these problems by providing an HFC-containing blowing agent comprising HFC-134.

Thus, in one aspect, the instant invention comprises a B-side, i.e., isocyanate-reactive composition, for preparing polyisocyanate foams, the composition comprising:

(a) a normally liquid active hydrogen-containing component having two or more active hydrogens and dissolved therein, at an effective temperature and pressure, an effective blowing agent amount of,

(b) an environmentally friendly normally gaseous polyfluorocarbon blowing agent devoid of halogen substituents other than fluorine and comprising a major proportion by weight of HFC-134, said B-side composition having a relatively low or no water content; such that the total water content corresponds to less than about 25 mole percent and the polyfluorocarbon blowing agent to more than about 75 mole percent of the combined water and polyfluorocarbon contents. Typically, the water content is less than about 15 mole percent, normally less than about 10 mole percent, still more desirably is substantially nil. Moreover, the polyfluorocarbon comprises at least about 70 weight percent, normally at least about 80 weight percent, still more desirably at least about 90 weight percent of HFC-134, including substantially 100 weight percent of this fluorocarbon. Normally, the blowing agent amount is about 5 to about 35, typically about 8 to about 30, and desirably about 10 to about 15 weight percent of the B-side composition consisting essentially of the blowing agent component and the active hydrogen-containing component.

Another aspect of the invention comprises a process for producing polyisocyanate-based foams, e.g., polyurethane and polyisocyanurate foams, including rigid closed-cell foams, which comprises effecting reaction of a polyisocyanate with an active hydrogen-containing compound bearing two or more active hydrogens, in the form of hydroxyl groups. For example, the process can be practiced while in the presence of a polyfluorocarbon blowing agent as defined above in the substantial absence of water as defined above. In one such process embodiment, the polyfluorocarbon component is preblended with the active hydrogen-containing component to form a substantially water-free and homogeneous isocyanate-reactive solution. The preblend is subsequently contacted with the polyisocyanate in a mixing zone of a conventional mixhead to form a substantially water-free reaction mixture, which in turn is allowed to expand at suitable temperatures and pressures to the foamed state. Alternatively, the blowing agent composition can be added to the hydrogen-containing

composition, in line to or separately at the mixhead and the subsequent isocyanate reactive solution introduced into the mixing zone by utilizing mixing techniques known in this art, and the resulting foam mixture is allowed to expand.

In yet another aspect, the invention relates to novel closed cell polyurethane and polyisocyanurate foams wherein the cells are substantially completely filled with a polyfluorocarbon blowing agent composition as defined above in the substantial absence of CO_2 as co-blowing agent. These novel foams can be produced in accordance with one or the other process embodiment described above.

By environmentally friendly polyfluorocarbon blowing agent composition comprising a major proportion of HFC-134 by weight, it is meant a blowing agent composition consisting of HFC-134 alone or containing less than about 50, normally less than about 30, and still more desirably less than about 10 weight percent of other compatible polyfluorinated blowing agents that are devoid of halogen substituents other than fluorine, and are not classified as VOCs (volatile organic compounds). That is, the blowing agent composition has low or zero ozone depletion potential (ODP) and low halocarbon global warming potential (HGWP) or greenhouse effect.

Suitable polyfluorinated co-blowing agents have 1 to 2 carbon atoms, at least one hydrogen atom and two or more fluorine atoms. Examples of suitable co-blowing agents comprise at least one member selected from the group consisting of HFC-134a (1,1,1,2-tetrafluoroethane), HFC-152a (1,1-difluoroethane), HFC-143a (1,1,1-trifluoroethane), HFC-32 (difluoromethane), HFC-125 (pentafluoroethane), among others. Especially useful blowing agent mixtures are those wherein the total number of fluorine atoms is equal to or exceeds the total number of hydrogen atoms so that the total composition is substantially nonflammable. Suitable blowing agent compositions include azeotrope-like or azeotropic mixtures of HFC-134 with said co-blowing agent or agents. For example, the flame resistant and nonflammable mixtures of HFC-134 with HFC-152a typically containing about 22 weight percent or less of HFC-152a, e.g., at least about 87 weight percent of HFC-134 and less than about 13 weight percent of HFC-152a.

By "nonflammable", it is meant to refer to such a determination made by test ASTM E 681-85 with modifications listed in draft form, Nov. 93, by ASTM committee E27 or by ASTM E918.

By "low HGWP" effect, it is meant to refer to a compound having a HGWP value of about 0.50 or less, preferably about 0.32 or less, more preferably about 0.30 or less as determined by the method described in D.A. Fisher et al, NATURE, 1990, 344, p. 513; hereby incorporated by reference.

The active hydrogen-containing compounds of this invention can comprise compounds having two or more groups that contain an active hydrogen atom reactive with an isocyanate group, such as described in U.S. Patent No. 4,394,491; hereby incorporated by reference. While any suitable compound can be employed, examples of such compounds have at least two hydroxyl groups per molecule, and more specifically comprise polyols, such as polyether or polyester polyols because such compounds can solvate HFC-134 and other hydrogen-containing polyfluorocarbon blowing agents as well as for the reactivity of hydroxyl groups towards isocyanate groups. While any suitable polyol can be employed, examples of such polyols are those which have an equivalent weight of about 50 to about 700, normally of about 70 to about 300, more typically of about 90 to about 270, and carry at least 2 hydroxyl groups, usually 3 to 8 such groups.

The saturated vapor pressure refers to the vapor pressure exerted by a solution of the blowing agent in an active hydrogen-containing component that is defined within a closed space. Given that the blowing agent is normally gaseous and, therefore, a lower-boiling compound than the normally liquid active hydrogen-containing component, the observed saturated vapor pressure at the temperature employed is substantially that of the blowing agent. The saturated vapor pressure of such solutions accordingly corresponds to the reaction pressure that would be required to maintain the blowing agent in solution, 1) in the same active hydrogen-containing composition, 2) at the same concentration and temperature, 3) as a substantially homogeneous mass, either as an isocyanate-reactive composition or as a foam-forming reaction mass containing a suitable polyisocyanate.

A key aspect of the instant invention is based upon the surprising discovery that HFC-134 is more highly soluble than its isomer HFC-134a in active hydrogen-containing compositions and that the resultant mixtures or solutions (B-side compositions) exert lower saturated vapor pressures than do comparable solutions of HFC-134a (and such other recommended blowing agent as HFC-152a over a wide range of temperatures and concentrations). Thus, preblends comprising practical

concentrations of HFC-134-based blowing agents may be formulated, maintained, and used in reactions with polyisocyanates under relatively more moderate conditions of temperature and pressure, including ambient, than are required for the other agents. HFC-134 may also be employed in the substantial absence of water as defined herein above. Thus, the higher solubilities and lower vapor pressures of HFC-134 in combination with the active hydrogen-containing substances makes more practical the formulation and use of B-side compositions containing HFC-134 for the production of polyisocyanate-based foams. This combination of properties also facilitates the process embodiments of bringing together and mixing the blowing agent, the active hydrogen-containing material and the polyisocyanate under foam-forming reaction conditions because lower operating pressures may be employed to produce desirably homogeneous reaction masses and resultant closed-cell foams.

BRIEF DESCRIPTION OF THE DRAWING

Figure 1 is a plot of the vapor pressures exerted by HFC-134, HFC-134a and HFC-152a from solution in a representative isocyanate-reactive polyol.

DETAILED DESCRIPTION

The instant invention relates to producing polyisocyanate-based foams utilizing selected combinations of blowing agents and active hydrogen-containing compositions, including isocyanate-reactive blends thereof, e.g., typically known in this art as B-side compositions. The invention also includes processes for producing polyurethane and polyisocyanurate closed-cell foams which comprise contacting a polyisocyanate with the active hydrogen-containing material under reaction conditions and while in the presence of the polyfluorinated blowing agent comprising a major weight proportion of HFC-134. The reactants may be brought together under reaction conditions separately, but substantially simultaneously, or, if the reactants are taken together, the blowing agent is such that it corresponds to less than about 25 mole percent water and greater than about 75 mole percent polyfluorocarbon blowing agent, e.g., less than 20 and normally less than about 10 mole percent water and the balance comprising polyfluorocarbon. It will be appreciated that some water in the reaction system is generally present when considering many of the active hydrogen-containing compositions, notably the polyether polyols, are

hygroscopic. The relatively low water levels defined herein are normally considered not to contribute any significant amounts of CO_2 to the foaming process. Active hydrogen-containing compounds useful in this invention include those that are normally liquid and have two or more groups that contain a hydrogen atom reactive with an isocyanate group. More specifically, suitable hydrogen-containing compounds have two or more hydroxyl groups per molecule and an equivalent weight of about 50 to about 700, normally about 70 to about 300 and desirably about 90 to about 270. Typically, suitable hydrogen-containing compounds are aliphatic and cycloaliphatic polyols carrying 2 to 16, more usually 3 to 8 hydroxyl groups.

While any suitable polyol or mixtures thereof can be employed in the instant invention, examples of suitable polyols comprise polyether polyols such as polyethylene oxides, polypropylene oxides, mixed polyethylene-propylene oxides with terminal hydroxyl groups, among others. Other suitable polyols can be prepared by reacting ethylene and/or propylene oxide with an initiator having 2 to 16, generally 3 to 8 hydroxyl groups as present, for example, in glycerol, pentaerythritol and carbohydrates such as sorbitol, glucose, sucrose and the like polyhydroxy compounds. Suitable polyether polyols can also include alaphatic or aromatic amine-based polyols. Aromatic polyester polyols may also be employed in the instant invention, e.g., those made by transesterifying polyethylene terephthalate (PET) scrap with a glycol such as diethylene glycol, or made by reacting phthalic anhydride with a glycol. The resulting polyester polyols may be reacted further with ethylene- and/or propylene oxide - to form an extended polyester polyol containing additional internal alkyleneoxy groups.

The inventive polyisocyanate-based foams can be prepared by contacting under reaction conditions at least one organic polyisocyanate with at least one active hydrogen-containing compound described hereinabove while in the presence of the polyfluorocarbon blowing agent also described hereinabove, with the latter two components preferably employed as an isocyanate-reactive preblend, e.g., B-side composition. The B-side composition of this invention can be prepared in any manner convenient to one skilled in this art, including simply weighing desired quantities of each component and, thereafter, combining them in an appropriate container at appropriate temperatures and pressures.

The concentration of the blowing agent relative to that of the active hydrogen-containing compound, whether used separately or as a preblend, is normally in the range of from about 5 to about 45 weight percent based on the total weight of these two components, more usually from about 8 to about 35, with from about 10 to at least about 25 weight percent preferred in most cases.

When preparing polyisocyanate-based foams, the polyisocyanate reactant is normally selected in such proportion relative to that of the active hydrogen-containing compound that the ratio of the equivalents of isocyanate groups to the equivalents of active hydrogen groups, i.e., the isocyanate index, is from about 0.9 to about 10 and in most cases from about 1 to about 4. The quantity of the blowing agent composition employed relative to that of the active hydrogen-containing composition is normally also selected within the above 5 to about 45 weight percent range effective to result in a foam whose overall density is in the range of from about 10 to about 500, normally from about 25 to about 100, and usually from about 25 to about 35 kilograms per cubic meter (kg/m^3) (wherein 1 kg/m^3 equals 0.062 pounds per cubic foot (pcf)).

While any suitable polyisocyanate can be employed in the instant process, examples of suitable polyisocyanates useful for making polyisocyanate-based foam comprise at least one of aromatic, aliphatic and cycloaliphatic polyisocyanates, among others. Representative members of these compounds comprise diisocyanates such as meta- or paraphenylene diisocyanate, toluene-2,4-diisocyanate, toluene-2,6-diisocyanate, hexamethylene-1,6-diisocyanate, tetramethylene-1,4-diisocyanate, cyclohexane-1,4-diisocyanate, hexahydrotoluene diisocyanate (and isomers), napthylene-1,5-diisocyanate, 1-methylphenyl-2,4-phenyldiisocyanate, diphenylmethane-4,4-diisocyanate, diphenylmethane-2,4-diissocyanate, 4,4 -biphenylenediisocyanate and 3,3-dimethyoxy-4,4 biphenylenediisocyanate and 3,3-dimethyldiphenylpropane-4,4-diisocyanate; triisocyanates such as toluene-2,4,6-triisocyanate and polyisocyanates such as 4,4 -dimethyldiphenylmethane-2,2,5,5-tetraisocyanate and the diverse polymethylenepoly-phenylopolyisocyanates, mixtures thereof, among others.

A crude polyisocyanate may also be used in the practice of this invention, such as the crude toluene diisocyanate obtained by the phosgenating a mixture comprising toluene diamines, or the crude diphenylmethane diisocyanate obtained by the phosgenating crude

diphenylmethanediamine. Specific examples of such compounds comprise methylene-bridged polyphenylpolyisocyanates, due to their ability to crosslink the polyurethane. The isocyanate index (ratio of equivalents of isocyanates to equivalents of active hydrogen-containing groups) is advantageously from about 0.9 to about 10, in most cases preferably about 1.0 to about 4.0.

It is often desirable to employ minor amounts of certain other ingredients in preparing polyisocyanate-based foams. Among these additional ingredients comprise one or members from the group consisting of catalysts, surfactants, flame retardants, preservatives, colorants, antioxidants, reinforcing agents, filler, antistatic agents, among others well known in this art.

Depending upon the composition, a surfactant can be employed to stabilize the foaming reaction mixture while curing. Such surfactants normally comprise a liquid or solid organosilicone compound. The surfactants are employed in amounts sufficient to stabilize the foaming reaction mixture against collapse and to prevent the formation of large, uneven cells. About 0.2 to about 5 parts or even more of the surfactant per 100 parts by weight polyol are usually sufficient.

One or more catalysts for the reaction of the polyol with the polyisocyanate may be also employed. While any suitable urethane catalyst may be employed, specific catalyst comprise tertiary amine compounds and organometallic compounds. Exemplary such catalysts are disclosed, for example, in U.S. Patent No. 5,164,419, which disclosure is incorporated herein by reference. For example, a catalyst for the trimerization of polyisocyanates, such as an alkali metal alkoxide, alkali metal carboxylate, or quaternary amine compound, may also optionally be employed herein. Such catalysts are used in an amount which measurably increases the rate of reaction of the polyisocyanate. Typical amounts are about 0.1 to about 5 parts of catalyst about per 100 parts by weight of polyol.

In one process of the invention for making a polyisocyanate-based foam, the polyol(s), polyisocyanate and other components are contacted, thoroughly mixed, and permitted to expand and cure into a cellular polymer. The mixing apparatus is not critical, and various conventional types of mixing head and spray apparatus are used. By conventional apparatus is meant apparatus, equiptment, and procedures conventionally employed in the preparation of isocyanate-based foams in which conventional isocyanate-based foam blowing agents, such as

fluorotrichloromethane (CCl_3F, CFC-11), are employed. Such conventional apparatus are discussed by: H. Boden et al. in chapter 4 of the Polyurethane Handbook, edited by G. Oertel, Hanser Publishers, New York, 1985; a paper by H. Grunbauer et al. titled "Fine Celled CFC-Free Rigid Foam - New Machinery with Low Boiling Blowing Agents" published in Polyurethanes 92 from the Proceedings of the SPI 34th Annual Technical/Marketing Conference, October 21-October 24, 1992, New Orleans, Louisiana; and a paper by M. Taverna et al. titled "Soluble or Insoluble Alternative Blowing Agents? Processing Technologies for Both Alternatives, Presented by the Equiptment Manufacturer", published in Polyurethanes World Congress 1991 from the Proceedings of the SPI/ISOPA September 24-26, 1991, Acropolis, Nice, France. These disclosures are hereby incorporated by reference. The low vapor pressure of B-side compositions containing blowing agent comprising HFC-134 allow such B-side compositions to be employed in isocyanated-based foam production in such conventional apparatus.

In another process of the invention, a preblend of certain raw materials is prepared prior to reacting the polyisocyanate and active hydrogen-containing components. For example, it is often useful to blend the polyol(s), blowing agent, surfactant(s), catalysts(s) and other components, except for polyisocyanates, and then contact this blend with the polyisocyanate. Alternatively, all the components may be introduced individually to the mixing zone where the polyisocyanate and polyol(s) are contacted. It is also possible to pre-react all or a portion of the polyol(s) with the polyisocyanate to form a prepolymer.

The invention composition and processes are applicable to the production of all kinds of expanded polyurethane foams, including, for example, integral skin, RIM and flexible foams, and in particular rigid closed-cell polymer foams useful in spray insulation as foam-in-place appliance foams, or rigid insulating board stock and in laminates.

EXAMPLES

The following examples are given to illustrate the invention and should not be interpreted as limiting it in any way. Unless stated otherwise, all parts and percentages are given by weight.

The following examples show the relative solubilities and associated vapor pressures of HFC-134 and HFC-134a in various polyether polyols over a range of temperatures and concentrations. The solubilities

are in weight percent of the polyfluorocarbon in solution in the polyol, and the vapor pressures exerted by the candidate blowing agent are expressed as saturated vapor pressures in pounds per square inch absolute (psia). The dissolution of the polyfluorocarbon in the polyol and the measurement of vapor pressures at the different concentrations and temperatures were conducted as follows:

SOLUBILITY TEST PROCEDURE

The solubility tests were run in a Fischer and Porter Glass Pressure Reaction Vessel. The polyol was added to the vessel and deaerated to eliminate the interference of air in the pressure measurements. Liquid HFC was then pressure added in increments and thoroughly mixed. At each increment, the solution was visually inspected for phase separation and vapor pressure was recorded. This was done in constant temperature bath at three (3) temperatures: 10°C, 25°C, 50°C. The limit of solubility was determined by the point at which two layers or an emulsion formed. The vapor pressure was measured after thoroughly mixing, and equilibrating temperature. The gauge pressure was converted to absolute pressure, PSIA, by correcting for barometric pressure. For comparison, following are: (a) the normal boiling points in degrees centigrade of HFC-134, HFC-134a and, for further reference, HFC-152a; and (b) the vapor pressures of these substances at 10, 25 and 50°C.

		Vapor Pressures, psia		
HFC	B.P. °C	10°C	25°C	50°C
134	-19.7	46.7	76.3	154.4
134a	-26.5	60.2	96.6	191.3
152a	-24.2	54.0	86.5	170.7

Example 1

Figure 1 is a graphical representation of wt.% blowing agent plotted vs. pressure. Figure 1 illustrates that HFC-134 exerts much lower saturated vapor pressures over the range of indicated concentrations in a sucrose based polyether polyol, polyol A, than either HFC-134a or HFC-152a, which translates into a higher degree of utility for HFC-134 as blowing agent for polyisocyanate-based foam production.

That the lower saturated vapor pressures of HFC-134 relative to those of HFC 134a, for example, are not attributable to its higher boiling point alone can be seen by comparing the ratios of the normal vapor

pressures of the two isomers at 25°C, viz. 76.3/96.6 = 0.79 against ratios of the saturated vapor pressures taken from Fig. 1 at 10, 15, 20 and 25 weight % of blowing agent at the same 25°C temperature, which ratios are: 18/25 = 0.72; 21/40 = 0.53; 35/65 = 0.54 and 40/75 = 0.53, respectively. The lower saturated vapor pressure ratios reflect the unexpected much higher degree of solvation of HFC-134 by the polyol, hence lower saturated vapor pressures. The same conclusions regarding solvation characteristics, hence blowing agent utility, can be drawn by comparing the saturated vapor pressures of HFC-134 versus those of HFC-152a, and of HFC-134a versus HFC-152a.

Example 2

This example compares the solubility and saturated vapor pressure characteristics of HFC-134 with those of HFC-134a in a blended polyether polyol normally used to make Intragal Skin Foam, Polyol B. The experimental data are given in Table 1.

The data further indicate the polyol-HFC-134 blend may be employed at lower pressures at ordinary temperatures over a higher range of blowing agent concentrations than comparable blends utilizing HFC-134a.

Example 3

The procedure of Examples 1 and 2 was repeated employing a propylene oxide polyether polyol, Polyol C. The saturated vapor pressure results are given in Table 2.

The data again establishes the superiority of HFC-134 over the HFC-134a isomer in that (1) the saturated vapor pressures exerted by HFC-134 are lower than those of HFC-134a at substantially all concentrations and temperatures, and (2) HFC-134 provides for homogeneous solutions over a greater range of concentrations and temperatures.

Example 4

The procedure of the previous examples was repeated with a sucrose polyether, Polyol A. The results are given in Table 3.

The superiority of the saturated vapor characteristics of the solutions of HFC-134 over those of HFC-134a over the range of concentrations and temperatures employed is evident from the tabulated data. For example, with HFC-134 at 25 weight percent concentration less

than 2 atmospheres pressure would be required to maintain solution at 10°C and less than 3 atmospheres at 25°C. In contrast, with HFC-134a at the same concentration, 3 atmospheres or more would be required at 10°C and 5 atmospheres or more at 25°C. The substantially lower pressure requirement of HFC-134 translates into a more economic process of using this isomer as blowing agent in combination with the active hydrogen component in a polyisocyanate foaming process.

Example 5

The procedure of the previous Examples was repeated using a sucrose amine based polyether polyol, Polyol D.

The saturated vapor pressure data are tabulated in Table 4 and again show the superiority of HFC-134 over HFC-134a in exerting much lower saturated vapor pressures over its blends with the polyol at all concentrations and temperatures employed, useful for the production of polyisocyanate-based foams.

Example 6

The solubility data (Table 5) demonstrate HFC-134 superior solubility with the aromatic-amine-type polyol, Polyol E, for polyisocyanate-based foam production. HFC-134a forms two phases at all the indicated concentrations and temperatures, while in contrast, HFC-134 forms homogeneous solutions over a broad range of concentrations and temperatures.

Example 7

This example compares the saturated vapor pressures of HFC-134 and HFC-134a mixtures with two typical aromatic polyester polyols. Polyol F is a phthalic anhydride based polyester, and Polyol G is a PET based polyester polyol.

The data in tables 6A and, 6B below again establish the greater solubility of the HFC-134 isomer in polyester type polyols.

TABLE 1
Polyol B (polyether blend)

wt.% HFC-134	Saturated Vapor Pressure (psia) 10°C	25°C	50°C	Comments
2.1	15	15	15	
4.5	15	15	15	
6.3	15	15	16	
8.4	15	15	21	
10.2	15	15	26	
12.4	15	15	31	
20.0	16	24	49	
25.1	20	31	60	
30.1	24	39	75	
35.2	27	46	78	
40.17	33	50	79	2 phases @ 50°C

wt.% HFC-134a	Saturated Vapor Pressure (psia) 10°C	25°C	50°C	Comments
2.4	15	15	15	
4.1	15	18	20	
5.8	15	15	27	
8.5	15	22	41	
10.1	20	25	47	
12.3	21	32	58	
20.5	31	50	93	
25.4	37	62	95	
30.2	42	67	101	
35.2	48	76	105	
41.2	53	87	125	2 phases @ 50°C

TABLE 2

Polyol C (propylene-oxide polyether)

wt.% HFC-134	Saturated Vapor Pressure (psia) 10°C	25°C	50°C	Comments
5.7	17	15	18	
10.6	19	19	33	
15.5	18	25	47	
20.6	23	34	61	
26.5	27	43	72	
30.1	31	48	79	
34.8	33	55	79	
40.2	37	57	84	

wt.% HFC-134a	Saturated Vapor Pressure (psia) 10°C	25°C	50°C	Comments
5.8	15	15	23	
8.1	22	24	36	
14.9	38	43	72	
21.9	43	64	103	
25.3	46	72	105	2 phases @ 50°C
33.3	52	83	115	2 phases @ all temperatures
40.3	58	90	119	2 phases @ all temperatures
47.7	60	94	147	2 phases @ all temperatures

TABLE 3

Polyol A (sucrose polyether)

wt.% HFC-134	Saturated Vapor Pressure (psia) 10°C	25°C	50°C	Comments
4.4	15	15	15	
10.9	15	17	34	
15.6	19	22	49	
20.3	23	35	64	
25.5	26	41	77	
30.0	29	47	79	
35.4	33	54	85	
40.1	34	60	85	

wt.% HFC-134a	Saturated Vapor Pressure (psia) 10°C	25°C	50°C	Comments
5.8	15	15	23	
8.1	22	24	36	
14.9	38	43	72	
21.9	43	64	103	
25.3	46	72	105	2 phases @ 50°C
33.3	52	83	115	2 phases @ all temperatures
40.3	58	90	119	2 phases @ all temperatures
47.7	60	94	147	2 phases @ all temperatures

TABLE 4

Polyol D (sucrose amine polyether)

wt.% HFC-134	Saturated Vapor Pressure (psia) 10°C	25°C	50°C	Comments	wt.% HFC-134a	Saturated Vapor Pressure (psia) 10°C	25°C	50°C	Comments
10.6	23	31	38		11.1	35	37	52	
14.9	23	26	42		12.4	37	38	56	
20.4	21	31	60		22.6	42	46	103	
25.4	24	38	75		23.9	42	61	105	
30.1	28	45	82		28.4	46	68	114	2 phases @ 50°C
35.3	31	53	84		34.2	51	80	115	2 phases @ all temperatures
40.1	34	55	85		42.0	57	88	122	2 phases @ all temperatures

TABLE 5
Polyol D (aromatic amine polyether)

wt.% HFC-134	Saturated Vapor Pressure (psia) 10°C	25°C	50°C	Comments
5.5	34	52	53	
10.0	34	54	60	
14.7	42	63	75	
20.0	40	60	86	
25.0	37	59	88	
30.1	39	67	89	
35.0	40	67	90	
40.0	39	71	88	2 phases @ 50°C

wt.% HFC-134a	Saturated Vapor Pressure (psia) 10°C	25°C	50°C	Comments
7.6	31	29	32	2 phases @ all temperatures
11.4	56	93	110	2 phases @ all temperatures
12.1	56	87	102	2 phases @ all temperatures
18.4	53	93	111	2 phases @ all temperatures

TABLE 6A

Polyol B (phthalic anhydride polyether)

wt.% HFC-134	Saturated Vapor Pressure (psia) 10°C	25°C	50°C	Comments
5.2	19	18	26	
10.4	23	24	51	
15.1	27	36	70	
19.9	29	47	84	
25.2	33	54	95	
30.2	35	60	87	
35.2	39	64	91	
40.1	40	62	97	

wt.% HFC-134a	Saturated Vapor Pressure (psia) 10°C	25°C	50°C	Comments
2.7	21	21	22	
14.0	38	71	101	2 phases @ 25&50°C
21.4	58	98	118	2 phases @ all temperatures
25.4	61	95	123	2 phases @ all temperatures
32.6	58	94	152	2 phases @ all temperatures
40.4	74	108	176	2 phases @ all temperatures

TABLE 6B

Polyol G (PET polyester)

wt.% HFC-134	Saturated Vapor Pressure (psia) 10°C	25°C	50°C	Comments
4.8	26	26	27	
10.6	19	22	47	
15.2	28	31	65	
20.3	27	41	81	
24.8	34	50	94	
30.3	33	58	90	
35.0	37	62	95	
40.1	38	65	96	

wt.% HFC-134a	Saturated Vapor Pressure (psia) 10°C	25°C	50°C	Comments
8.1	50	51	55	
13.0	55	70	89	2 phases @ 10&25°C
20.2	59	94	100	2 phases @ 10&25°C
26.8	60	96	136	2 phases @ all temperatures
34.1	57	90	123	2 phases @ all temperatures
37.4	57	90	152	2 phases @ all temperatures

Example 8

The following example illustrates use of HFC-134 to produce a typical rigid pour-in-place insulation foam. These foams were produced on a Gusmer Delta Rein 40, at a foam throughput of 20.21 lbs/minute and component feed temperatures at 21-27 °C. The low vapor pressure of the B-side composition employing HFC-134 allowed preparation of this foam in conventional apparatus.

FOAM FORMULATION

Component	Parts by Weight	
MDI Isocyanate[1]	150	150
Polyether Polyol Blend[2] (including silicone surfactant and catalyst)	100	100
HFC-134 Blowing Agent	19.6	-
HFC-134a Blowing Agent	-	18.1

Properties

Isocyanate Index (x100)	130	130
B-side System Vapor Pressure (PSIG)	0[3]	25
Foam Density (lbs/ft^3)	1.8-1.9	1.8-1.9
Thermal Conductivity (BTU•in/ft^2•hr•°F)	0.156-0.165	0.160-0.164
Cell Structure	fine & uniform	fine, slight pinholes, occasional void

1-Low viscosity polymeric methylene diphenyl diisocyanate with an equivalent weight of 136.
2-Sucrose-based polyether polyol with a hydroxyl value in the 325-350 range.
3-As typical in conventional foam apparatus, a slight nitrogen pressure was used to feed the metering pumps.

FL-1004

THE FOLLOWING IS CLAIMED:

1. A process for producing a closed-cell polyurethane or polyisocyanurate polymer foam comprising

reacting an isocyanate-containing component with an active hydrogen-containing component having two or more active hydrogens in the presence of a blowing agent comprising HFC-134, wherein said blowing agent is dissolved in said active-hydrogen containing component forming a homogenous solution, and

forming said closed-cell polyurethane or polyisocyanurate polymer foam in conventional apparatus for preparation of isocyanate-based foam in which conventional isocyanate-based foam blowing agents, such as fluorotrichloromethane (CCl_3F, CFC-11), are employed.

2. A process for producing a closed-cell polyurethane or polyisocyanurate polymer foam containing within its cells a gaseous blowing agent comprising HFC-134, characterized in that said foam is formed by allowing an isocyanate-containing component to react with an active hydrogen-containing component having two or more active hydrogens in the presence of a blowing agent comprising HFC-134, wherein

said blowing agent is dissolved in said active-hydrogen containing component forming a homogenous solution, and

wherein the ratio of the saturated vapor pressure of said blowing agent above said homogenous solution to the saturated vapor pressure of blowing agent above an identical homogeneous solution containing HFC-134a as blowing agent in place of said HFC-134, is less than the ratio of the normal vapor pressure of said blowing agent to the normal vapor pressure of HFC-134a.

3. The process of claims 1 or 2 wherein the ratio of the saturated vapor pressure of said blowing agent above said homogenous solution to the saturated vapor pressure of blowing agent above an identical homogeneous solution containing HFC-134a as blowing agent in place of said HFC-134, is at least 5% less than the ratio of the normal vapor pressure of said blowing agent to the normal vapor pressure of HFC-134a.

4. The process of claims 1 or 2 wherein said blowing agent is devoid of halogen substituents other than fluorine and further comprises at least one co-

blowing agent selected from the group consisting of HFC-32, HFC-152a, HFC-143a, HFC-134a, and HFC-125.

5. The process of claims 1 or 2 wherein HFC-134 accounts for at least about 70 mol% of the total blowing agent contents and water accounts for less than about 25 mole% of the total blowing agent contents.

6. The process of claims 1 or 2 wherein said active hydrogen containing component is at least one polyol selected from the group consisting of polyether polyols, polyester polyols, and polyhydroxy-terminated acetal resins.

7. A homogenous B-side composition for the preparation of polyisocyanate-based polymer foams, comprising

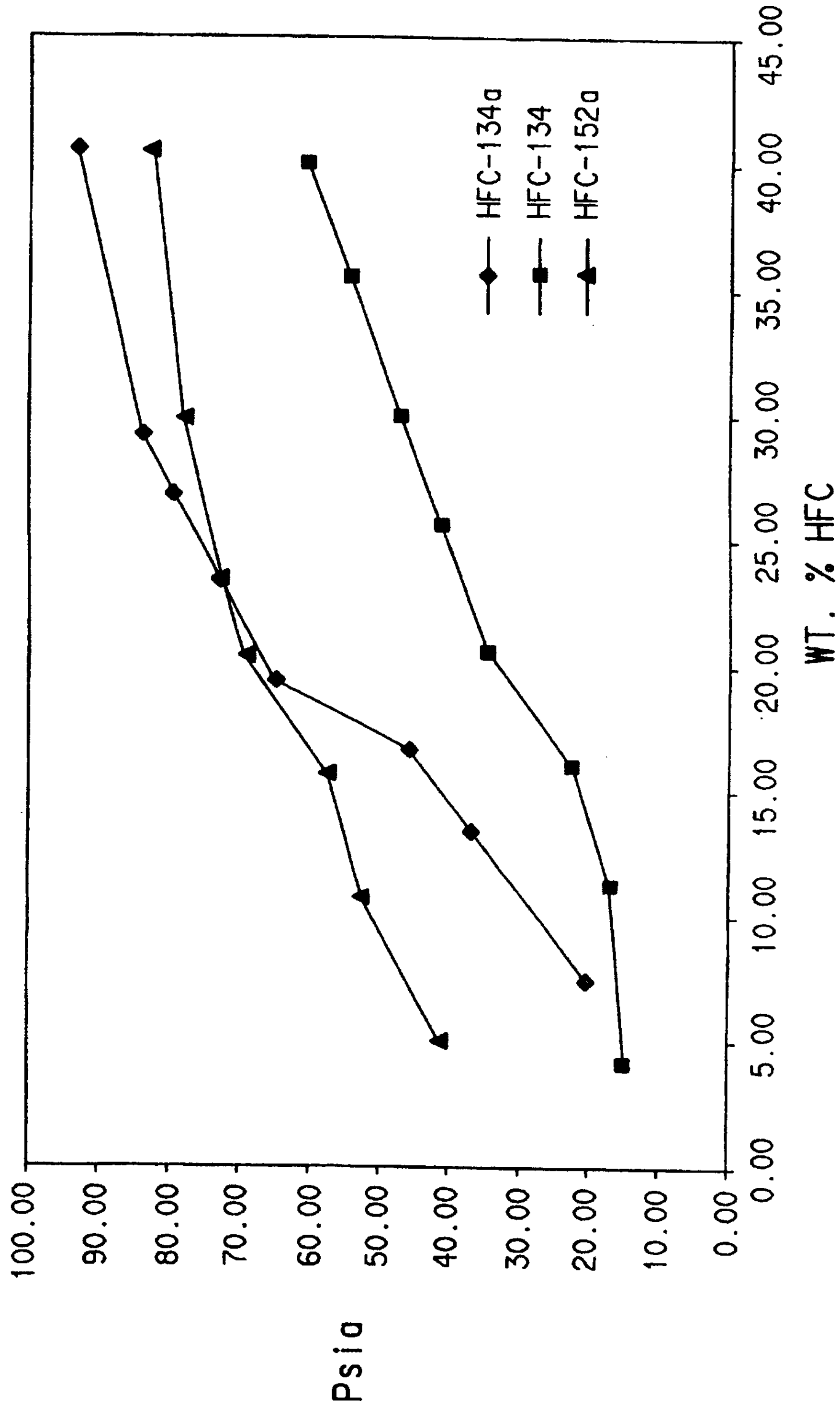
a) a liquid active hydrogen-containing component having two or more active hydrogens, and

b) a gaseous blowing agent comprising HFC-134 dissolved in said active hydrogen-containing component, wherein

said blowing agent is devoid of halogen substituents other than fluorine, and

said B-side composition comprises homogeneous solutions comprising said blowing agent and said active hydrogen-containing component under conditions where an identical B-side composition, containing HFC-134a in place of HFC-134, is a heterogeneous mixture.

FIG. 1


HFC-134a
HFC-134
HFC-152a
WT. % HFC
Psia
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5.00
10.00
15.00
20.00
25.00
30.00
35.00
40.00
45.00
0.00
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INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 97/13073

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C08J9/14 //C08L75:04

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C08J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 91 12289 A (DOW CHEMICAL CO) 22 August 1991 see page 8, line 32 - page 9, line 7	1,6-8
X	see page 9, line 31 - page 10, line 2 see claims 1,2,7,8 ---	4
A	WO 92 17558 A (DU PONT) 15 October 1992 see claims -----	1-7

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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1

Date of the actual completion of the international search	Date of mailing of the international search report
18 November 1997	09/12/1997

Name and mailing address of the ISA	Authorized officer
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INTERNATIONAL SEARCH REPORT

Information on patent family members

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PCT/US 97/13073

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